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MATERIALS REPORT 103

**MECHANISMS OF HYDROGEN EMBRITTLEMENT—
CRACK GROWTH IN A LOW-ALLOY
ULTRA-HIGH-STRENGTH STEEL UNDER CYCLIC AND
SUSTAINED STRESSES IN GASEOUS HYDROGEN**

by

S. P. LYNCH and N. E. RYAN

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SUMMARY

Rates of crack growth in a low-alloy ultra-high-strength steel (D6aC) under cyclic and sustained stresses have been measured as functions of stress-intensity, for different cyclic wave-forms and frequencies, in low pressure (13.3 kPa) hydrogen, dry air, and vacuum (10^{-3} Pa) environments; sustained-load cracking in liquid mercury was also studied.

Frequency and wave-form had large effects on rates of fatigue-crack growth in hydrogen but little influence on fatigue in air and vacuum. For triangular wave-forms, rates of crack growth in hydrogen were determined mainly by the stress-intensity range and the load-rise time. For square-wave loading, rates of crack growth in hydrogen were proportional to the time at maximum load. Quantitative relationships between rates of cracking under sustained and cyclic loads were not found.

Many similarities between hydrogen-embrittlement and liquid-metal embrittlement (e.g. surfaces of the intercrystalline fractures induced by hydrogen and mercury were sometimes indistinguishable) suggested that the mechanism of embrittlement is basically the same in both cases. It is considered that previous explanations for embrittlement are not consistent with the present fractographic observations (e.g. dimpled transcrystalline fractures were sometimes observed after crack growth in mercury and hydrogen). The present results suggest that the effects of hydrogen and liquid-metal environments on crack growth can generally be explained on the basis that chemisorption influences interatomic bonds/spacings at surfaces (crack tips) and thereby facilitates nucleation of dislocations at crack tips. Some aspects of hydrogen embrittlement are discussed in terms of the proposed model.

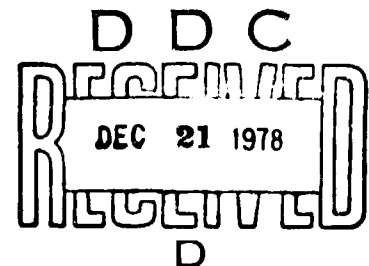
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1. INTRODUCTION

In high-strength steels, hydrogen environments induce sub-critical crack growth under sustained stress and can increase the rates of crack growth under cyclic stress markedly beyond those in inert environments. Some aspects of these and other effects of hydrogen on the behaviour of materials are discussed in references 1 and 2. The present studies of crack growth as a function of stress intensity under (a) cyclic stress in 'inert' environments (fatigue), (b) cyclic stress in hydrogen ('corrosion-fatigue'), (c) sustained stress in hydrogen, and (d) sustained stress in liquid mercury were undertaken to investigate possible relationships between these cracking processes. If relationships between (a), (b), and (c) above could be established, they would provide a basis for using existing data on fatigue and sustained-load cracking to predict rates of 'corrosion-fatigue' without the necessity for empirical testing. It was also considered that the results would be relevant to understanding mechanisms of hydrogen-assisted crack growth.

2. EXPERIMENTAL

Specimens were manufactured from 22 mm thick D6aC steel plate of the following composition:

C	Mo	Cr	Ni	V	Mn	Si	P	S	Fe
0.46	1.2	1.1	0.6	0.12	0.8	0.24	0.004	0.002	rem. wt. %

They were austenitised at 930°C, quenched in molten salt at 520°C ('Ausbay' region), held at 520°C for 25 min., quenched in molten salt at 210°C, and then double-tempered at 550°C for 2 hr. This heat-treatment produces a tempered-martensitic (predominantly lath-type) microstructure. Mechanical properties were as follows:

0.2% Proof Stress	UTS	Elongation	Reduction of Area	K_{Ic}
(MPa)	(MPa)	%	%	(MPa m ^{1/2})
1460	1650	12	43	78

A few sustained-load tests in liquid mercury were also carried out on specimens additionally tempered at either 625°C for 4 hr. or 650°C for 4 hr giving proof stresses of ~1250 MPa and ~1000 MPa, respectively.

Crack growth in the gaseous environments was studied using tapered double-cantilever-beam (DCB) specimens. For this specimen geometry, the crack-tip stress intensity is independent of crack length over a considerable portion of the specimen. Specimens were enclosed in an environmental chamber which could be evacuated to 10^{-3} Pa and then filled with gases. High purity hydrogen with O₂, N₂, and H₂O contents of less than 10, 100, and 200 ppm respectively, and dry air with a water-vapour content of less than 25 ppm were used. Hydrogen gas was chosen as a 'model' aggressive environment which induces less complex conditions at crack tips than aqueous media, where electrochemical reactions could produce a variety of effects. A hydrogen pressure of 13.3 kPa was used, giving rates of fatigue-crack growth (which increase with increasing pressure) in the range 0.1 to 100 μ m per cycle; slower and faster rates are wasteful of testing time and specimens, respectively.

Specimens were tested at 25°C using a closed-loop electrohydraulic machine operating under load control. Rates of fatigue-crack growth (da/dN) were measured as a function of stress-intensity range (ΔK), for a stress ratio of ~0.1, in dry air, vacuum (10^{-3} Pa) and hydrogen (13.3 kPa) using four wave-forms and four to five frequencies, from 5 Hz to 0.02 Hz. The wave-forms used were (a) triangular (Δ), (b) 'positive' saw-tooth (∇), (c) 'negative' saw-tooth (∇), with loading-to-unloading times in the ratios 1:1, 10:1, and 1:10 respectively, and (d) 'square' (\square) with loading/unloading times ~0.02 sec. Rates of crack growth were determined from direct observation of crack lengths on the sides of specimens and also by compliance

measurements—a calibration curve of crack-opening displacement versus crack length had been established previously.

Sustained-load cracking in liquid mercury (at 25°C) was studied using parallel-sided bolt-loaded DCB specimens at constant crack-opening displacement (COD), for which the crack-tip stress intensity decreases with increasing crack length. Mercury was applied to specimens by drilling a small shallow hole through a pool of mercury just ahead of the chevron notch. On loading, fracture initially occurred in air under continuously increasing COD until the crack tip intersected the area 'wetted' by mercury; rapid sub-critical crack growth, under a constant COD, then occurred. Mercury was removed from the fracture by evaporation in vacuum at ~100°C. Fracture surfaces were examined by scanning-electron microscopy and transmission-electron microscopy of secondary-carbon replicas.

3. RESULTS

3.1 Crack-Growth Data

In dry air and vacuum, frequency and wave-form had little effect on rates of crack growth under cyclic stress at constant ΔK ; differences between rates of crack growth in air and vacuum were small. Plotting da/dN versus ΔK on log scales, the air and vacuum data fell within a narrow scatter band which approximated to a linear relationship over the range of stress intensity between ~20 and ~60 MPa m^{1/2} (Fig. 1a-d); tests in hydrogen were restricted to this range of ΔK . The hydrogen environment produced large crack-growth rates, compared with the 'inert' environments, which were very sensitive to wave-form and frequency (Fig. 1a-d—each point is the average of at least three tests.) For given stress intensities and wave-forms, a decrease of two orders of magnitude in frequency produced an increase of roughly one order of magnitude in rate of crack growth, with increases being a little larger at higher ΔK . For given stress intensities and frequencies, rates of crack growth increased with waveform in the order going from \square to Δ to \triangle to \square . The influence of frequency and wave-form (except for \square) could be rationalised approximately on the basis that rates of crack growth in hydrogen (for a given ΔK) were proportional to the rise-time (i.e. crack-opening time) (Fig. 2); crack-closing time had some effect since, for the same rise-time, \square wave forms (slow unloading rates) generally produced significantly faster crack growth than \triangle or Δ wave-forms. The predominant effect of rise-time on rates of crack growth has been reported for other materials and environments.^(3,4) Rates of crack growth under sustained load in hydrogen and mercury environments are shown as functions of stress intensity in Figure 3; crack growth in mercury was two to three orders of magnitude faster than in (13.3 kPa) hydrogen. For \square wave-forms, where crack growth occurs under both sustained and rising loads, rates of crack growth per cycle were proportional to the time at maximum load (Fig. 4).

3.2 Fractography

3.2.1 Sustained-load Cracking in Hydrogen

Gradual changes in the appearance of the fracture-surfaces with gradually changing stress intensity were observed. At 'low' stress intensities (20–30 MPa m^{1/2}), crack growth was intercrystalline (i.e. along prior-austenite grain boundaries) and fairly smooth intercrystalline facets were observed. At 'intermediate' stress intensities (40–50 MPa m^{1/2}), many intercrystalline facets exhibited tear ridges and dimples (Fig. 5a,b). At 'high' stress intensities (65–75 MPa m^{1/2}), fractures were predominantly transcrystalline with dimpled surfaces (Fig. 6a,b). (Overload fracture—above K_{Ic} ~78 MPa m^{1/2}—was also dimpled and transcrystalline (Fig. 6c)). Similar observations have been reported for other steels cracked in gaseous hydrogen.⁽⁵⁾

3.2.2 Sustained-load Cracking in Liquid Mercury

Intercrystalline facets, virtually indistinguishable from those produced in hydrogen at 'intermediate' stress intensity, were observed (Fig. 7a,b), but there was little change in fracture-surface appearance† with stress intensity. For specimens additionally tempered to a lower

† The solubility of iron in mercury is negligible and, hence, fracture-surface topography is probably not affected by the presence of mercury on fracture surfaces.

strength (~ 1250 MPa) than 'usual' (all other tests used specimens with a proof stress of ~ 1460 MPa), sub-critical crack growth in liquid mercury produced a mixed transcrystalline/intercrystalline fracture with both areas almost entirely dimpled (Fig. 8a,b). For specimens tempered to a proof stress of ~ 1000 MPa, sub-critical crack growth in liquid mercury did not occur.

3.2.3 Fatigue in Dry Air

Crack growth was transcrystalline for all stress-intensities. At 'intermediate' ΔK ($30\text{--}50$ MPa $m^{1/2}$), quite well-defined fatigue striations were observed in some areas (Fig. 9); numerous steps, ridges, and small dimples were also observed and, hence, striations in many areas were short, irregular, and not well-defined. At low ΔK ($20\text{--}30$ MPa $m^{1/2}$), fracture surfaces were similar to those just described but striations were more difficult to resolve; at high ΔK (>60 MPa $m^{1/2}$), dimples predominated.

3.2.4 Fatigue in Hydrogen

Fracture-surface appearance depended on frequency and wave-form as well as on ΔK . At low ΔK and slow rates of loading, flat intercrystalline facets similar to those produced under sustained loading were observed. As rates of loading and ΔK increased, intercrystalline facets showed more evidence of local ductility (tear ridges, dimples) and the extent of transcrystalline cracking increased. Striations, although not well-defined, were evident in transcrystalline areas and on some intercrystalline facets. (Fig. 10).

4. DISCUSSION

4.1 Previous Explanations for Hydrogen Embrittlement (HE)

There is fairly general agreement⁽¹⁾ that the mechanism of HE of steels is the same regardless of the source of hydrogen. However, none of the previously proposed mechanisms of HE is generally accepted since none accounts for all the observations.⁽⁶⁾

One of the earliest theories for HE was based on precipitation of hydrogen at internal defects (e.g. voids, 'weak' particle/matrix interfaces); it has been proposed^(7,8) that the pressure developed by this precipitation is added to the applied stress and thus lowers the apparent fracture stress. This phenomenon probably contributes to embrittlement in 'charged' specimens but, by itself, does not account for many aspects of embrittlement.

Most mechanisms of HE have been based on supposed effects of **dissolved** hydrogen on the iron lattice. The most often-cited explanation, proposed by Oriani⁽⁹⁾ (expanding on theories by Troiano⁽¹⁰⁾ and others), is that dissolved hydrogen accumulates in regions of very high elastic stress within a few atomic distances from crack tips and thereby reduces the cohesive strength of the lattice. This hypothesis is based mainly on observations that hydrogen-induced failures often show little evidence of plastic deformation and result in flat intercrystalline or cleavage fracture facets. (In inert environments, crack growth is commonly associated with considerable deformation and often involves nucleation and growth of microvoids ahead of crack tips—dimpled fracture surfaces are often observed—and it is generally accepted that fracture occurs by slip processes at crack tips). In some cases, however, the presence of hydrogen can reduce tensile ductility without a change in fracture mode—only a change in dimple size is observed.⁽¹¹⁾ Similarly, Beachem⁽⁵⁾ observed that sub-critical crack growth of steels in gaseous hydrogen produced entirely dimpled fracture surfaces in some circumstances. He concluded that hydrogen-induced crack growth occurred by slip processes rather than by 'decohesion' and suggested that flat cleavage/intercrystalline facets also resulted from fracture by microscopic plasticity processes that were not readily apparent. Beachem therefore proposed that hydrogen diffused into the lattice just ahead of crack tips and there aided whatever deformation processes the lattice would allow. There is evidence that dissolved hydrogen may influence slip but generalizations about its effect are difficult to make; hydrogen may induce both increases and decreases in flow stress in different circumstances.⁽⁶⁾ Overall, it might be expected that dissolved hydrogen would not influence slip sufficiently to promote crack growth, since (a) hydrogen is quite mobile and can probably be swept along by moving dislocations⁽¹²⁾, and (b) there is already a high concentration of immobile solutes (and precipitates) in steels.

Many workers⁽¹³⁻¹⁶⁾ have noted that embrittlement of materials by hydrogen is similar to

liquid-metal embrittlement (LME). It has been proposed⁽¹⁶⁾ that chemisorption of liquid-metal or hydrogen atoms lowers the tensile (cohesive) strength of atomic bonds at crack tips so that crack growth occurs by repeated adsorption and tensile separation of bonds. The case for a common mechanism for HE and LME, based on chemisorption, is supported by the present studies. However, a 'reduced-cohesion' mechanism is *not* consistent with all the experimental observations and a new theory which explains both LME and HE is proposed here. (§ 4.3)

4.2 Comparison of HE and LME

Similarities between HE and LME are:

- (a) The hydrogen/iron couple has many of the characteristics of most liquid-metal/solid-metal embrittlement couples, viz. low mutual solubilities, little tendency to form compounds, similar electronegativities and strong binding energies between adsorbate and solid.⁽¹⁸⁾
- (b) Intercrystalline fractures are characteristic of both HE and LME, and fracture surfaces are indistinguishable in some cases (Figs 5, 7); dimpled transcrystalline fractures are sometimes observed after both HE and LME (Figs 6a, b; 8a, b).
- (c) The severity of both types of embrittlement generally increases with increasing strength. Steels with strengths above $\sim 1,200$ MPa are particularly susceptible to HE; for D6aC steel, sub-critical crack growth in mercury was not observed below about this strength in the present work.
- (d) The segregation of 'temper-embrittlement' elements (e.g. S, P, Sb, As, Sn) to prior-austenite grain boundaries enhances intercrystalline embrittlement by hydrogen and liquid metals.^(17, 18)
- (e) The addition of elements which form stable compounds with the solid to an embrittling liquid metal inhibits LME, e.g. the addition of a small amount of barium to mercury reduces the embrittlement of zinc by mercury.⁽¹⁹⁾ Similarly, traces of oxygen in the hydrogen inhibits HE.⁽²⁰⁾
- (f) The temperature-sensitivities of HE and LME are similar—maximum embrittlement generally occurs at a particular temperature, with reduced embrittlement at higher and lower temperatures.^(14, 16, 21)
- (g) Changes in the slip characteristics of the material from wavy glide to coplanar glide increases the severity of both HE and LME.^(22, 23)
- (h) Rates of crack growth about the same as those observed for D6aC steel in mercury have been reported⁽²⁴⁾ for a similar steel in partially dissociated hydrogen.

Known differences between HE and LME, e.g. much faster rates of crack growth in mercury compared to molecular hydrogen, increasing susceptibility to HE (but not LME) with decreasing strain rates, could arise because transport and adsorption kinetics are different. Other phenomena peculiar to HE, e.g. sub-surface initiation and growth of cracks, rates of crack growth controlled by diffusion of hydrogen through the lattice in some circumstances, do not necessarily indicate a different mechanism from LME since hydrogen could diffuse to, and chemisorb at, tips of internal cracks. Thus, it is concluded that HE and LME probably occur by the same basic process.

4.3 A new explanation for HE and LME

Crack growth occurs by either (a) tensile separation (decohesion) of atoms or (b) shear movement of atoms at crack tips, i.e. nucleation (and subsequent movement) of dislocations from crack tips, or emergence of dislocations at crack tips. For many materials, in inert environments, crack growth occurs by slip and the plastic strain is sufficient to produce some blunting at crack tips and to cause initiation and growth of voids ahead of cracks. Thus, crack growth involves coalescence of microvoids with crack tips and, as a result, dimpled fracture surfaces are observed. The present observations show that sub-critical crack growth of steel in liquid mercury and in hydrogen produces entirely dimpled fracture surfaces in some circumstances (Figs 6, 8), although dimples are generally smaller and shallower than those observed after fracture in air. Metallographic and fractographic observations of LME in other materials (e.g. aluminium single crystals)⁽²⁵⁾ show that considerable slip occurs around crack tips during crack growth in embrittling liquid-metal environments (much more deformation occurs in air) and that entirely dimpled fracture surfaces are produced. Thus, in many cases, crack growth

in embrittling environments almost certainly occurs by plastic flow rather than by decohesion of atoms at crack tips*. Furthermore, since transitions from dimpled to 'flat' fracture surfaces occur gradually (dimples become shallower and smaller and the proportion of fracture surface covered by dimples gradually decreases) with decreasing stress intensity or increasing strength, it is more probable that 'flat' fracture surfaces (Figs 5, 7) also result from crack growth by slip processes rather than by 'decohesion'. 'Flat' fracture surfaces would be observed (a) if dimples were too small/shallow to be resolved (the formation of dimples below the limit of resolution of replica techniques is quite probable), or (b) if fracture occurred by alternate shear at crack tips with insufficient strain ahead of cracks to nucleate voids. Beachem⁽⁵⁾ has also proposed that hydrogen-assisted crack growth occurs by plastic flow, as already mentioned.

LME is almost certainly caused by an effect of chemisorption at crack tips; mutual solubilities of LME couples are often negligible and rates of crack growth are so rapid (e.g. steel-mercury) that other processes would not have time to occur. The many similarities between LME and HE (4.2) suggest a common mechanism and it is proposed that sub-critical crack growth in liquid-metal/hydrogen environments, by plastic flow, can be explained on the basis that chemisorption of liquid-metal/hydrogen atoms facilitates nucleation of dislocations at crack tips. Atoms at surfaces (crack tips), in vacuum, have fewer neighbours than atoms in the interior and, hence, the lattice spacings in the first few atomic layers differ from those in the interior⁽²⁸⁾; such 'surface-lattice distortion' should hinder the nucleation (and egress) of dislocations at surfaces⁽²⁹⁾. Since chemisorption of environmental species effectively increases the number of neighbours around surface atoms, 'surface-lattice distortion' should be reduced⁽³⁰⁾ and nucleation of dislocations at surfaces (crack tips), should be facilitated by adsorption. Observations⁽³¹⁾ of iron-alloy surfaces in the presence of hydrogen, using field-ion microscopy, do indeed suggest that nucleation of dislocations is activated by adsorption of hydrogen.

4.4 Explanation of some aspects of HE

4.4.1 Environmental factors—effect of oxygen, solute elements on HE

The present considerations suggest that susceptibility to HE/LME (for a given stress intensity and microstructure) should be greater for larger chemisorption-induced reductions in 'surface-lattice distortion'; increased coverage by adsorbed species should also favour embrittlement since longer (surface) dislocation sources, which probably require lower activation stresses, may then be nucleated. Thus, the life of adsorbates on surfaces before reactions (such as compound formation, dissolution, diffusion into the solid) occur should influence the surface coverage at a particular instant and, hence, the nucleation of dislocations. An effect of surface coverage could account for the influence of hydrogen pressure, strain rate, temperature, and the presence of oxygen on HE. For example, the inhibition of HE by traces of oxygen in hydrogen environments probably occurs because oxygen adsorbs preferentially and rapidly produces an oxide at crack tips; oxygen itself does not facilitate crack growth, probably because its life in the adsorbed state is not long enough to produce a significant surface coverage by adsorbed oxygen at a particular instant. Chemisorption of species other than liquid-metal/hydrogen atoms could possibly facilitate generation of dislocations and some cases of stress-corrosion cracking could be explained on this basis.

The propensity for intercrystalline cracking in hydrogen/liquid-metal environments could be explained by preferential chemisorption of environmental species at grain boundaries. The presence of a high concentration of solute elements at prior-austenite boundaries could also be significant since the presence of such elements (S, As, P, Sb, Sn) can, by themselves, produce intercrystalline (temper-) embrittlement. Tin and antimony produce embrittlement (of steels) when in their liquid-metal state, and it is possible that temper-embrittlement, LME, and HE could all be manifestations of the same phenomenon (i.e. adsorption—activated dislocation

* It has been suggested⁽⁹⁾ that small areas of local plasticity could arise during fracture by 'decohesion', by plastic tearing of ligaments, unaffected by the environment, between advancing lobes of main cracks. However, it is very unlikely that crack growth occurs by a mixture of plastic flow and 'decohesion' to produce entirely dimpled fracture surfaces. Several workers^(26,27) have commented that, for fracture in general, crack growth by tensile separation of atoms at crack tips is probably uncommon.

nucleation) with differences arising because the source, mobility and 'potency' of embrittling species differ. A common mechanism would explain the 'co-operative' interaction between temper-embrittlement and HE/LME.

4.4.2 Ductile versus brittle behaviour

Previous considerations of ductile and brittle behaviour⁽³²⁾ have usually been based on a ' σ/τ ratio' criterion, where σ is the tensile stress required to rupture interatomic bonds at crack tips and τ is the shear stress required to move dislocations on slip planes intersecting crack tips. This criterion, however, only differentiates the relative tendencies for fracture by tensile separation of atoms and fracture by shear movement of atoms. Hence, it is considered inapplicable to those cases where both ductile and 'brittle' fracture occur by slip. Here, the distribution of slip around crack tips during crack growth should determine fracture behaviour. Extensive blunting at tips of cracks, in specimens below general yield, requires a general strain in the plastic zone around cracks and, hence, generally necessitates slip on at least five independent systems which freely interpenetrate and cross-slip⁽³³⁾; crack growth by (alternate) shear requires slip on only two slip planes intersecting crack tips.⁽³⁴⁾ The balance between crack growth and crack-tip blunting (both relax elastic strain energy around cracks) should therefore be determined by the relative proportions of slip on planes intersecting crack tips compared to 'general' slip ahead of cracks. Adsorption-activated nucleation (and subsequent movement) of dislocations from crack tips promotes the former and, hence, favours crack growth rather than crack-tip blunting*. Thus, increments of fatigue-crack growth, for given crack-opening displacements, are larger in hydrogen environments than in inert environments and both cyclic and sustained-load fractures in hydrogen have a 'less-ductile' appearance than fractures in inert environments. For sustained-load fracture, the amount of 'general' slip decreases with (a) more effective adsorption-induced generation of dislocations, (b) decreasing stress-intensity, and (c) increasing strength. The extent of void nucleation and growth ahead of cracks also decreases and, hence, fracture-surface dimples are either smaller/shallower or not observed (Figs 5-8). Where dimples are observed, they are often elongated, in the direction of crack growth, (Fig. 8a) probably due to the preferential advance of 'external' cracks (growth promoted by adsorption) towards internal voids (growing in vacuum—unless hydrogen diffuses or is swept by dislocations into voids). On fatigue-fracture surfaces, well-defined striations are observed after crack growth in air but *not* after cracking in hydrogen (Figs 9, 10). In many materials, 'brittle' striations are often observed after fatigue in 'aggressive' environments (e.g. hydrogen-charged iron⁽³⁵⁾, liquid-metal environments/aluminium⁽³⁶⁾, aqueous media/aluminium alloys) while 'ductile' striations are generally observed after fatigue in inert environments. Striations are often found on fatigue-fracture surfaces probably because, during unloading, slip behind the crack tip deforms part of the fracture surface produced during loading. Since crack-growth increments and crack-tip profiles are influenced by the environment, striation profiles are also affected (as illustrated in Fig. 11). Distributions and densities of dislocations adjacent to fracture surfaces should also be different after fatigue in inert and aggressive environments; observations consistent with the proposed model have been reported⁽³⁷⁾ for a nickel alloy fatigued in hydrogen and vacuum.

4.4.3 Effect of hydrogen on rates of crack growth

For fatigue in inert† environments, it is well-established that crack growth occurs only during loading as a result of slip at crack tips. Analyses of plastic-blunting/alternate-shear processes^(34, 38) show that crack-growth increments per cycle, da/dN , should be proportional to crack-tip-opening displacements, ΔCOD . Thus, $da/dN = B \cdot \Delta COD$; $COD \propto K^2/\sigma_y E$, and, hence, $da/dN \propto K^2$ relationships are often approximately observed (Fig. 1). The constant B can be considered as a measure of the balance between crack growth and crack-tip blunting during

* The effects of chemisorption on the lattice are 'screened out' within a few atomic distances of the surface and, hence, chemisorption does not influence the stress required for 'general' slip or usually affect properties other than fracture.

† Although there were probably very slight environmental effects in 'dry' air and 'vacuum', these environments were considered to be inert relative to hydrogen.

tensile loading. Thus B , and hence da/dN , depends on the environment (chemisorption), stress intensity, microstructure, etc. The influence of rise-time and stress intensity on rates of crack growth in hydrogen (Figs. 1, 2) can be explained on the basis that the effectiveness of hydrogen in promoting crack growth depends on the surface (crack-tip) coverage by adsorbed atoms during crack growth (4.4.1). Hydrogen transport/adsorption is less able to keep up with crack growth, and surface coverage is less, for higher rates of crack growth, da/dt ; in other words, B is smaller for faster loading rates and higher stress intensities.

The correlation between rates of crack growth and rise-time (Fig. 2) breaks down to some extent in that, for the same-rise time, \square wave-forms generally result in faster crack growth than \triangle and ∇ wave-forms. This effect probably occurs because the rates of unloading have a slight influence on crack growth. Since initial unloading displacements are elastic, there is probably a pause after peak load before reverse plastic deformation occurs around crack tips; crack growth during a pause of the order of 2% of the unloading period (estimated from square-wave data) would account for the results.

Other factors to be considered are the influence of environment on (a) the 'effective' COD , i.e. the range of COD over which plastic flow occurs—this should be greater in hydrogen than in air/vacuum, and (b) the amount of crack closure—dislocation egress behind crack tips during unloading could be affected by the environment and this, in turn, could influence crack growth.

4.4.4 Relationships between Sustained- and Cyclic-Load Cracking

It has been suggested^(39, 40) that rates of 'corrosion-fatigue' can be obtained by adding a component due to fatigue in an inert environment to an environmental component computed from the sustained-load-cracking data and the cyclic-load profile. For \triangle , \square , and ∇ wave-forms, crack-growth rates predicted by this 'superposition' analysis were quite different from the measured rates, e.g. predicted rates were about five times too slow at low ΔK . Various modifications to the 'superposition' analysis did not reveal any simple correlation between rates of sustained- and cyclic-load cracking, suggesting that there was a synergistic interaction (more marked at lower ΔK) between environment and rising load. (Similar results have been reported for other environment-material systems.) Quantitative correlations would not be expected on considering that increments of crack growth during fatigue and 'corrosion-fatigue' are controlled by increments of crack-opening displacement, while sustained-load cracking occurs under a constant COD . However, since cracking in hydrogen under both cyclic and sustained load probably involves adsorption-activated slip, qualitative relations between these processes should usually be observed, e.g. environmental factors which produce faster sustained-load cracking should also increase rates of 'corrosion-fatigue'.

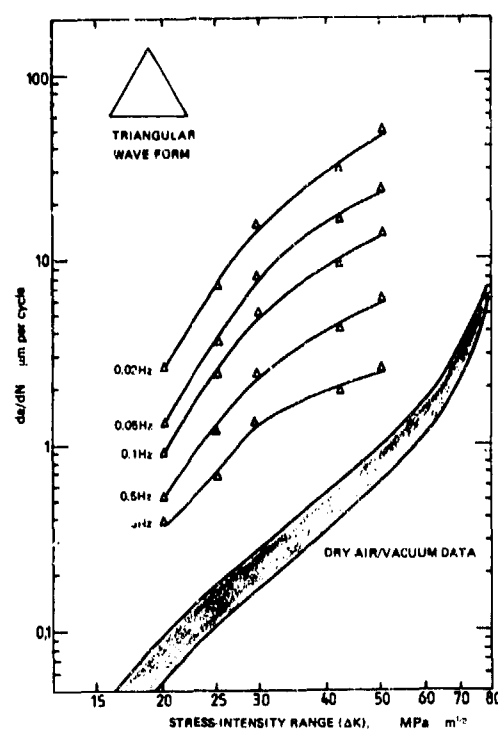
For square-wave loading, rates of fatigue-crack growth in hydrogen could be predicted to some extent by adding a 'corrosion-fatigue' component (i.e. crack growth during rising load in hydrogen) to a sustained-load cracking component (crack growth during the hold time at K_{max}). (Crack growth does not occur at K_{min} which is less than $K_{I_{sc}}$.) Predicted rates were in reasonable agreement with measured rates at low ΔK but were two to three times too high at high ΔK . The discrepancy at high ΔK probably occurs because the effective hydrogen pressure at the crack tip after a rapid increment of crack growth during rising load is lower than the nominal hydrogen pressure. Residual stresses around crack tips during sustained and cyclic-load crack will also be different and could influence rates of crack growth.

5. CONCLUSIONS

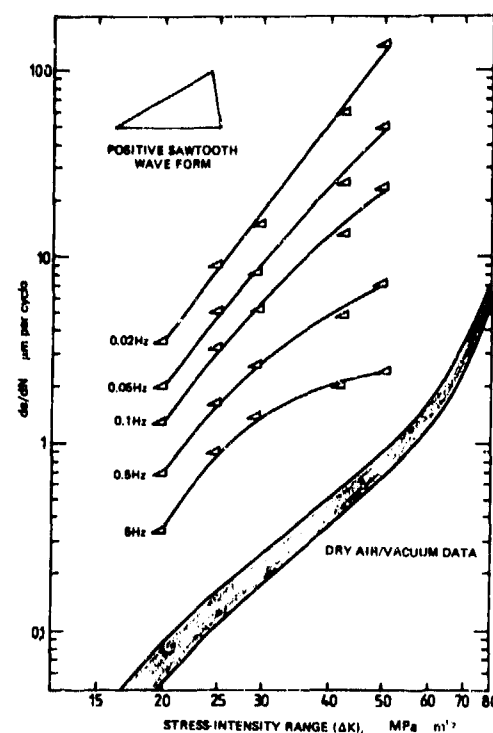
1. Comparison of hydrogen embrittlement and liquid-metal embrittlement suggests a common mechanism of crack growth.
2. Observations indicate that crack growth in embrittling environments generally occurs by plastic flow rather than by 'decohesion' of atoms.
3. Hydrogen embrittlement and liquid-metal embrittlement can be explained on the basis that chemisorption of hydrogen/liquid-metal atoms facilitates nucleation of dislocations at crack tips.
4. Rates of fatigue-crack growth in hydrogen are proportional to rise-times (rates unloading have only small effects); quantitative correlations between rates of cyclic- and sustained-load cracking were not observed.

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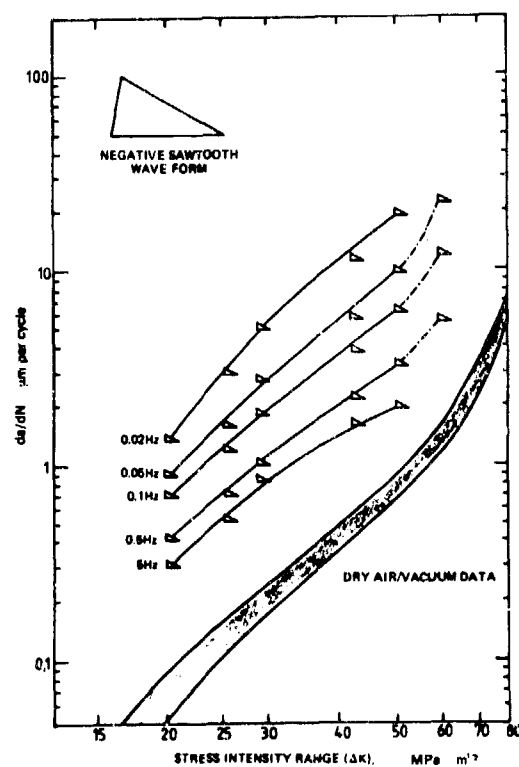
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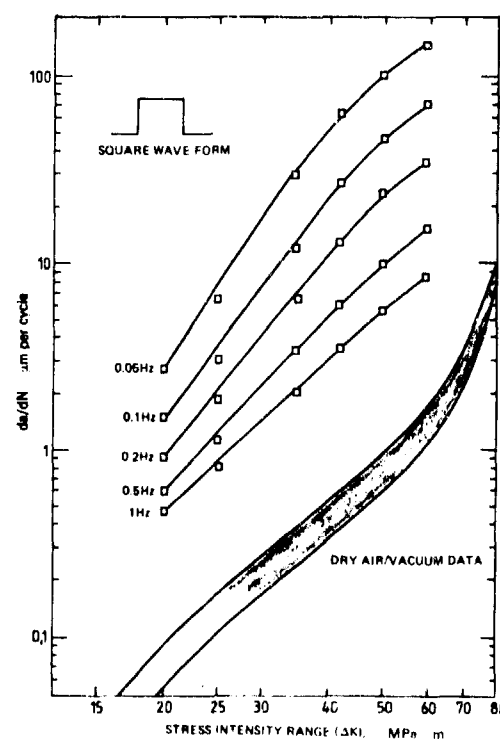
(a)



(b)



(c)



(d)

Fig. 1. Graphs of rate of fatigue-crack growth per cycle (da/dN) versus stress-intensity range (ΔK) showing effect of cyclic frequency for (a) triangular-wave forms, (b) positive-sawtooth-wave forms, (c) negative-sawtooth-wave forms, and (d) square-wave forms, in a hydrogen gas environment. Rates of crack growth in dry air and vacuum (shaded band) are relatively insensitive to frequency and wave form.

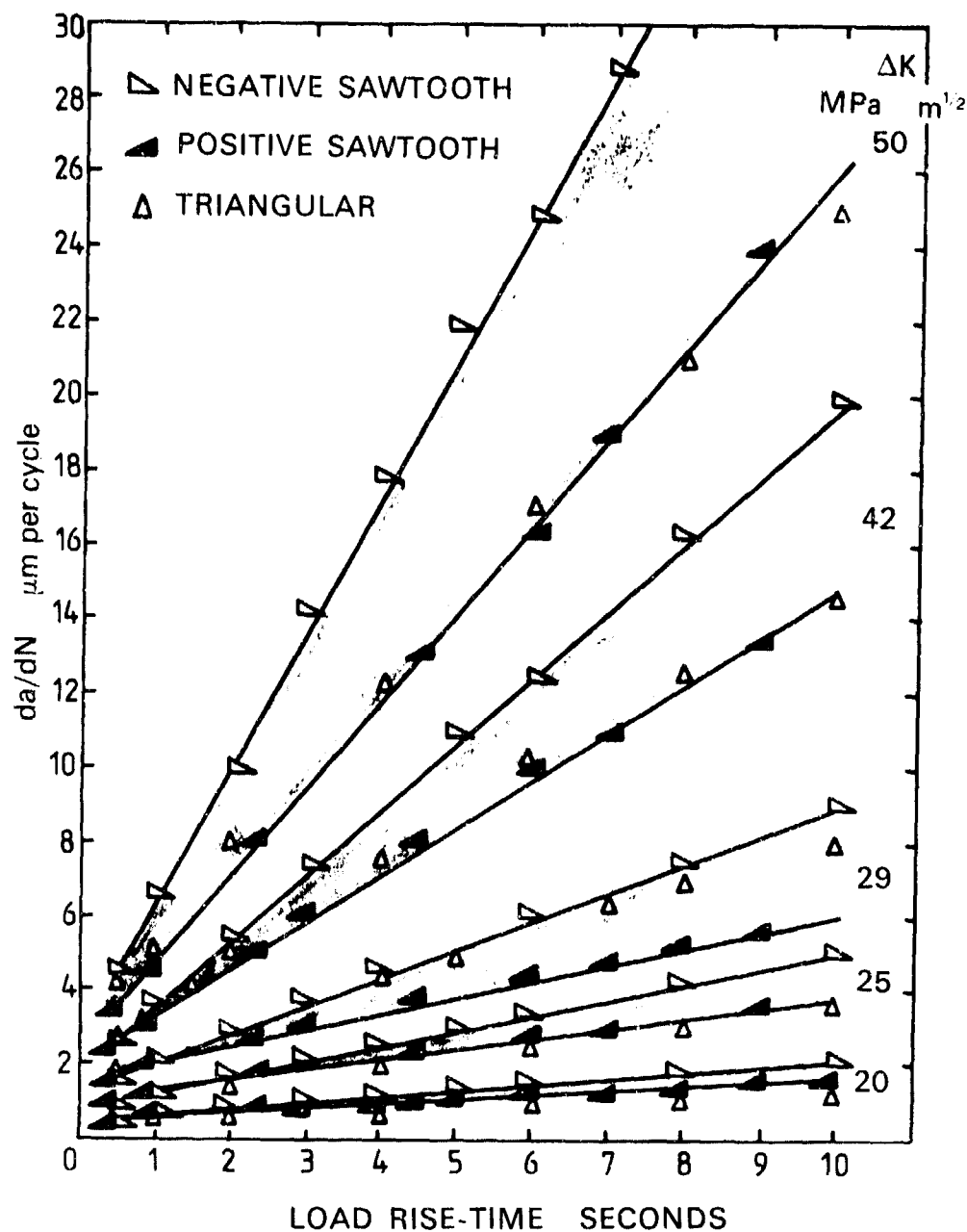


Fig. 2 Graph of rate of fatigue-crack growth per cycle (da/dN), in hydrogen gas, versus load-rise time showing that, for a given ΔK , da/dN is approximately proportional to the rise-time. Rates of unloading have a small effect in that, for the same rise times ∇ wave forms generally produce slightly faster crack growth than \blacktriangle or \triangle wave forms.

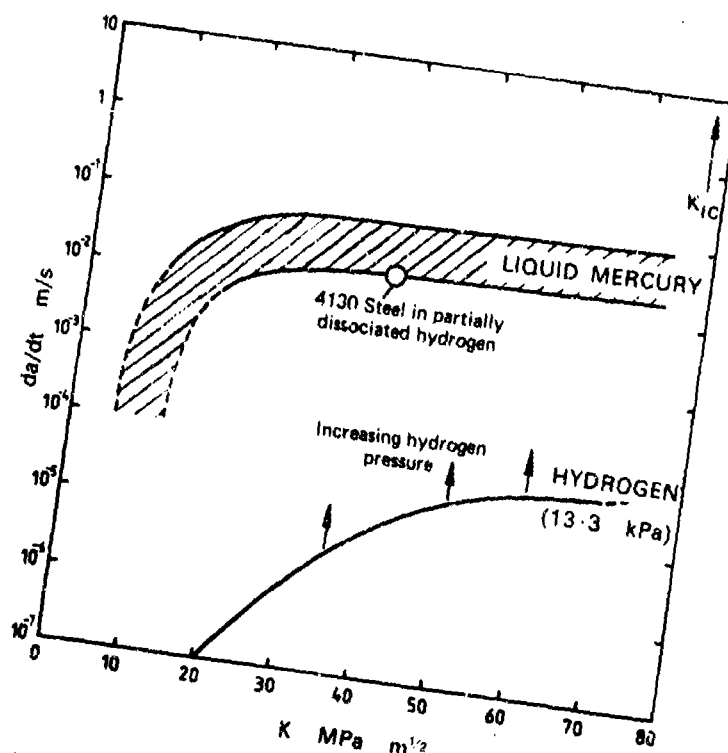


Fig. 3 Effect of stress intensity (K) on rates of sustained-load crack growth (da/dt) in low pressure (13.3 kPa) hydrogen and liquid mercury environments.

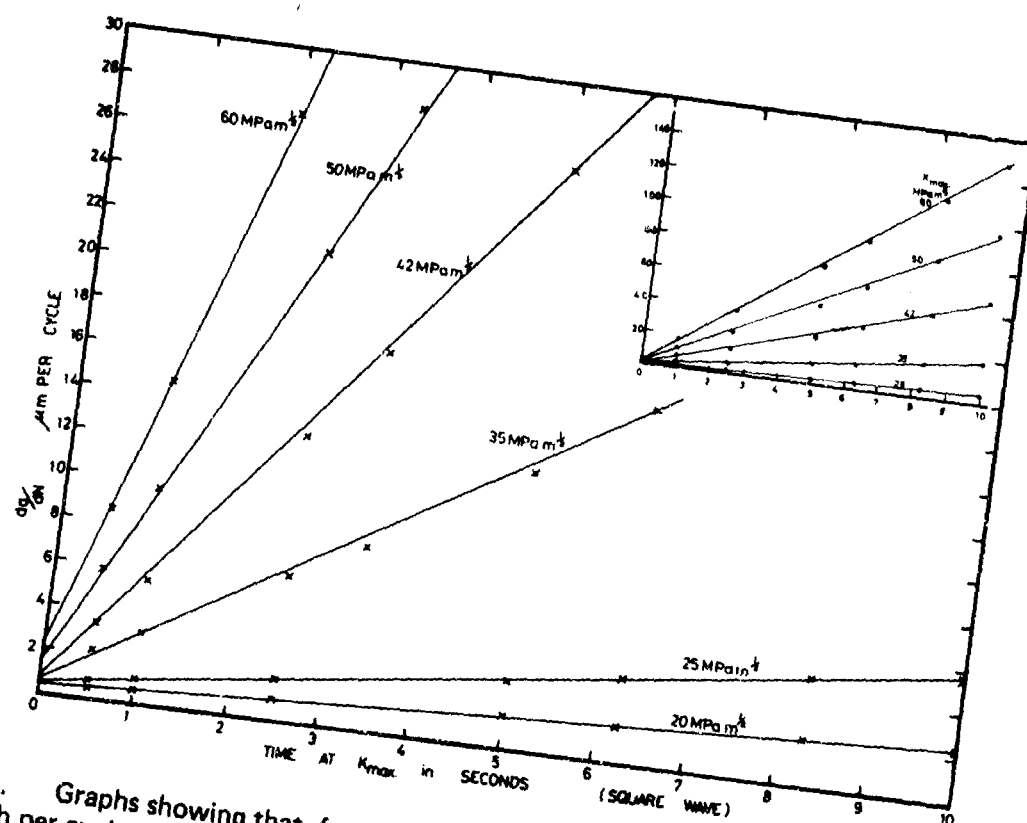
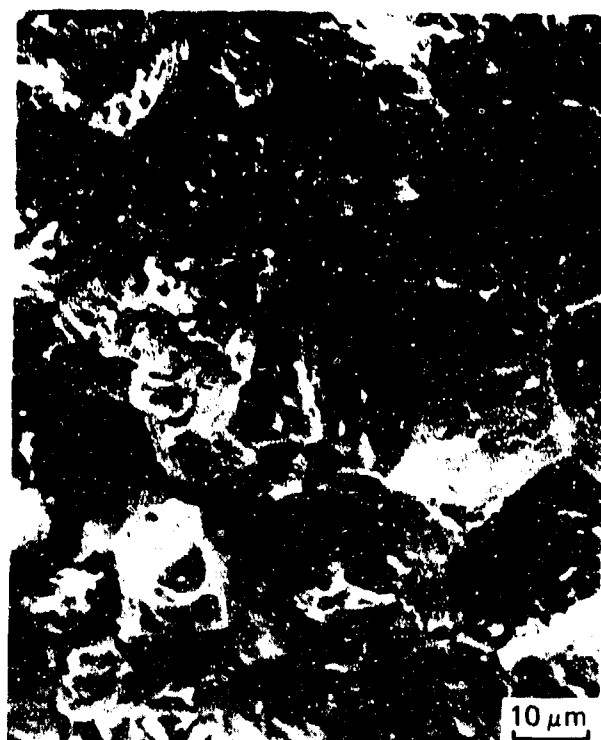


Fig. 4. Graphs showing that, for square-wave cycling in hydrogen, rates of fatigue-crack growth per cycle (da/dN) for a given ΔK are proportional to the time at K_{max} .



(a)

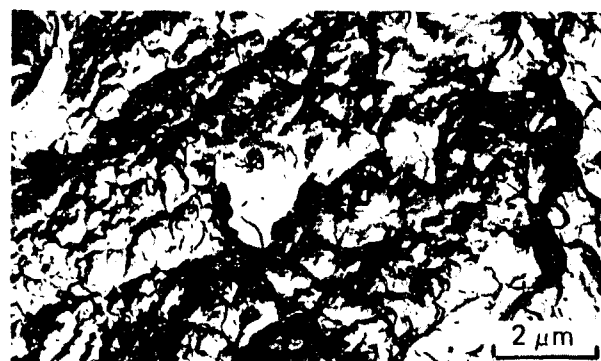


(b)

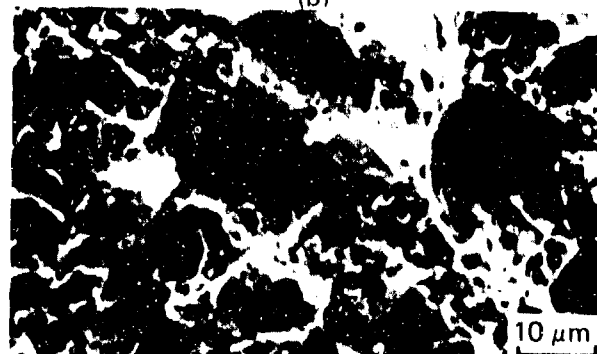
Fig. 5. Fractographs ((a) — SEM, (b) — EM) after sustained-load cracking in hydrogen at 'intermediate' stress intensities ($40 - 50 \text{ MPa m}^{1/2}$) showing flat and dimpled intercrystalline facets.



(a)



(b)



(c)

Fig. 6. Fractographs (a) — SEM, (b) — EM after sustained-load cracking in hydrogen at high stress intensities ($65 - 75 \text{ MPa m}^{1/2}$) showing predominantly dimpled transcrystalline fracture; (c) — SEM shows dimpled transcrystalline fracture produced by overload in dry air ($K_{IC} - 78 \text{ MPa m}^{1/2}$).



(a)



(b)

Fig. 7. Fractographs ((a) – SEM, (b) – EM) after sub-critical crack growth in liquid mercury at 'intermediate' stress intensities showing intercrystalline facets indistinguishable from those produced by cracking in hydrogen (cf. Fig. 5 a, b).



(a)



(b)

Fig. 8. Fractographs (EM) after sub-critical crack growth in liquid mercury at intermediate stress intensities for a specimen tempered to a lower strength than 'normal' (see text) showing (a) area of dimpled transcrystalline fracture and (b) area of dimpled intercrystalline fracture.

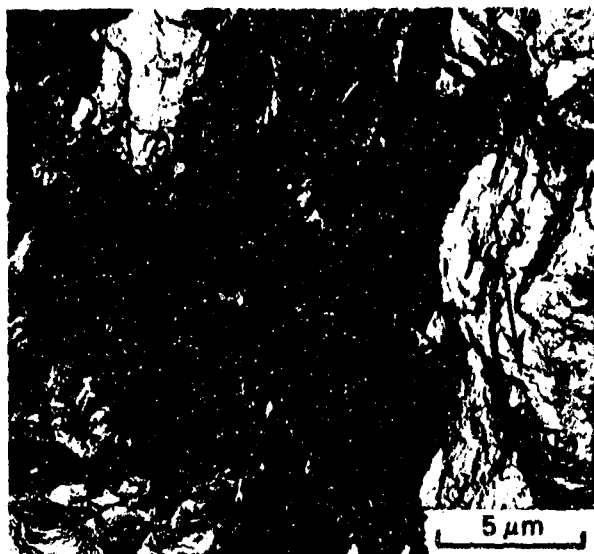


Fig. 9. Fractograph (EM) after fatigue-crack growth in dry air ($\Delta K = 35 \text{ MPa m}^{1/2}$) showing striations, small dimples and tear ridges.

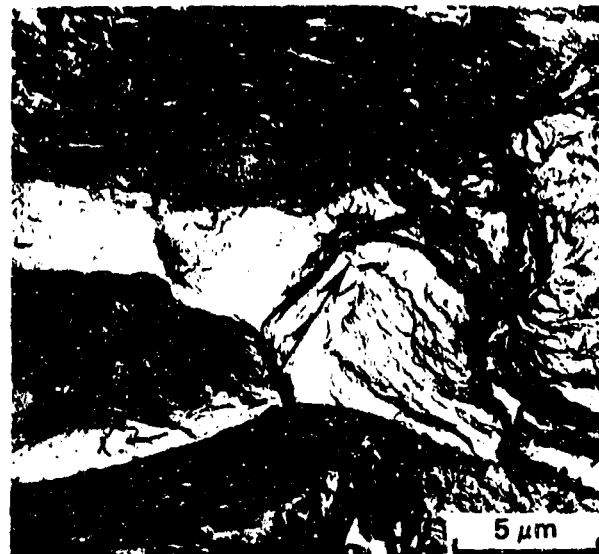


Fig. 10. Fractograph (EM) after fatigue crack growth in hydrogen ($\Delta K = 25 \text{ MPa m}^{1/2}$, 1 Hz, Δ wave-form) showing intercrystalline and transcrystalline areas with signs of striations in both regions.

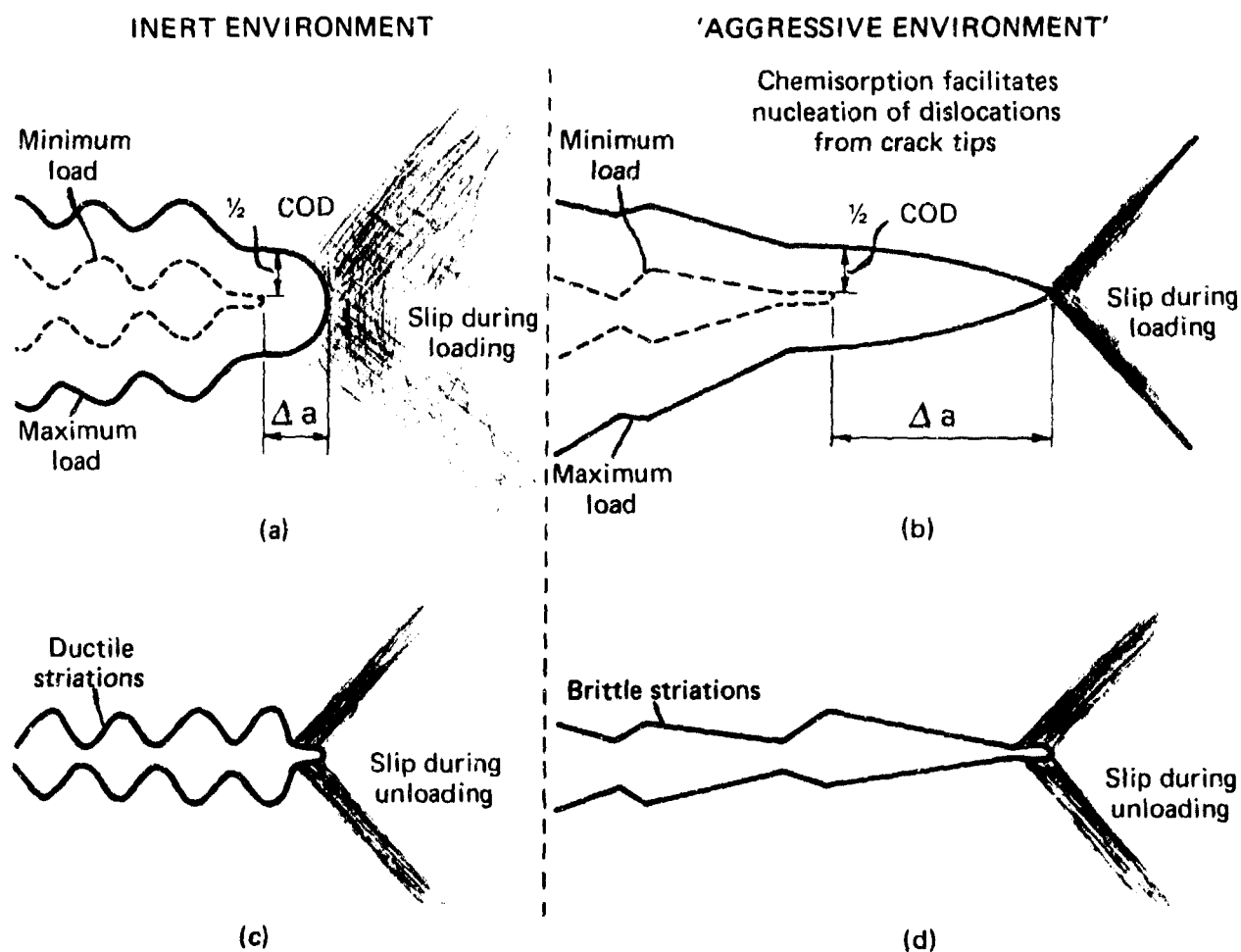


Fig. 11. a, b. Diagrams illustrating effect of environment on slip distribution around crack tips, crack-tip profiles, and crack-growth increments per cycle (Δa) for the same crack-tip-opening displacements (ΔCOD) during fatigue-crack-growth. During unloading, slip behind crack tips produces (c) 'ductile' striations, and (d) 'brittle' striations, on fracture surfaces.

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16. ABSTRACT

Rates of crack growth in a low-alloy ultra-high-strength steel (D6aC) under cyclic and sustained stresses have been measured as functions of stress-intensity, for different cyclic wave-forms and frequencies, in low pressure (13.3 kPa) hydrogen, dry air, and vacuum (10^{-3} Pa) environments; sustained-load cracking in liquid mercury was also studied.

Frequency and wave-form had large effects on rates of fatigue-crack growth in hydrogen but little influence on fatigue in air and vacuum. For triangular wave-forms, rates of crack growth in hydrogen were determined mainly by the stress-intensity range and the load-rise time. For square-wave loading, rates of crack growth in hydrogen were proportional to the time at maximum load. Quantitative relationships between rates of cracking under sustained and cyclic loads were not found.

Many similarities between hydrogen-embrittlement and liquid-metal embrittlement (e.g. surfaces of the intercrystalline fractures induced by hydrogen and mercury were sometimes indistinguishable) suggested that the mechanism of embrittlement is basically the same in both cases. It is considered that previous explanations for embrittlement are not consistent with the present fractographic observations (e.g. dimpled transcrystalline fractures were sometimes observed after crack growth in mercury and hydrogen). The present results suggest that the effects of hydrogen and liquid-metal environments on crack growth can generally be explained on the basis that chemisorption influences interatomic bonds/spacings at surfaces (crack tips) and thereby facilitates nucleation of dislocations at crack tips. Some aspects of hydrogen embrittlement are discussed in terms of the proposed model.

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